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Calcite-sea water reactions and CO_2 storage in ocean surface waters

CALCITE-SEAWATER REACTIONS AND CO_2 STORAGE IN OCEAN SURFACE WATERS

R. Wollast
Oceanography Laboratory
University of Brussels
Brussels, Belgium

R. M. Garrels
F. T. Mackenzie
Department of Geological Sciences
Northwestern University
Evanston, Illinois 60201

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Abstract

The behavior of calcite in typical mixed-layer seawater (Bermuda seawater) supersaturated with respect to calcite and aragonite was investigated using saturometry techniques. Additions of reagent-grade calcite to this seawater produce a surface film on the calcite that is more soluble than calcite. The observed increase in solubility of the film, expressed as $-\log IAP_{CaCO_3}$ (IAP = Ion Activity Product), varies directly with increase in thickness, and probably Mg content, of the precipitated carbonate. Dissolution of these precipitates in seawaters undersaturated with them was rapid.

We suggest from the results of these experiments that suspended calcite in the ocean mixed layer may be coated with carbonate films. As the concentration of CO_2 in the atmosphere increases owing to the burning of fossil fuels and other activities of society, and the CO_2 content of the mixed layer also increases, carbonate coatings on calcite should begin to dissolve before aragonite and calcite. Furthermore, if these reactions involving CO_2 and carbonates are globally significant, then models of the global balance of CO_2, that assume no uptake of CO_2 by reactions with solids in the oceans until aragonite saturation is reached, may be significantly in error.

Introduction

It is commonly assumed that the increase of CO_2 in the atmosphere is accompanied by increased dissolved CO_2 in the mixed layer of the ocean. It is further assumed that the increase of CO_2 in the ocean is entirely related to increased solubility of gaseous CO_2 in seawater, and that there is no significant dissolution of carbonate minerals that would augment uptake by the mixed layer. This second assumption is based upon many measurements of the saturation states of low magnesian calcite (henceforth called calcite) and of aragonite in the shallow marine waters that show supersaturation with respect to both phases.

The assumption of lack of reaction of increased CO_2 with carbonate minerals is open to two major possible errors: first, there may be very large areas in high latitudes where both calcite and/or aragonite are dissolving in undersaturated mixed-layer waters (cf. Alexandersson, 1976, 1978; Berner, 1977), but where few measurements of saturation state have thus far been made; second, carbonates with higher solubilities than calcite or aragonite may respond to CO_2 change.

This article is devoted largely to studies of the behavior of calcite (< 1 mole % $MgCO_3$) in typical mixed-layer seawater--namely seawater from the shallow waters of Bermuda, which are continuously supersaturated with respect to calcite and aragonite. In addition to revealing some aspects of the behavior of calcite, we use this article as a vehicle for demonstrating some of the pitfalls faced by investigators of carbonate-seawater reactions.

Review of Some Reactions of Calcite with Seawater

Waters of the mixed layer of the intermediate- and low-latitude oceans are commonly supersaturated three- to four-fold with respect to calcite. This supersaturation persists even if the seawater is in contact with shallow water sediments and suspended materials containing abundant calcite. Berner (1975) demonstrated that a supersaturation of about 400% (degree of saturation = 100 x ratio of ion activity product of Ca^{++} and $CO_3^{=}$ in seawater to the equilibrium value = 100 IAP/K_e) is required for a finite rate of carbonate precipitation on calcite seed materials in seawater of average composition. Pytkowicz (1965) showed that homogeneous nucleation of carbonates is strongly inhibited by the magnesium concentration of seawater. A number of investigators (cf. Chave, 1965, and Chave and Suess, 1967) found that the pH lowering caused by the addition of calcite to seawater is dependent on surface area. Weyl (1965), in a series of excellent experiments, showed that as seawater is progressively neutralized in the presence of calcite grains, the first precipitate has a solubility about the same as that of the calcite, but that subsequent precipitates formed from supersaturated waters have higher solubilities.

There is a continuing controversy concerning the reasons for the inhibition of the growth of calcite in supersaturated seawater--whether it is dominated by organic coatings, by phosphate adsorption, or by a magnesium effect. We consider that the work reported here represents nearly time-independent relations between solution and solids, whatever the explanation of our observations.

General Experimental Procedure

Measurements: Measurements of pH were made with a Corning 130 digital read-out pH meter, using a combination glass--saturated calomel electrode, and were recorded on a Varian paper strip recorder. The meter is quite stable; checks on a pH 7 buffer over periods of 24 hours seldom showed drifts of more than a few thousandths of a pH unit. The precision of the measurements is estimated to be within $\pm$ 0.005 pH units. Laboratory temperatures fluctuated a few degrees, with a mean close to 25°C; consequently, temperature corrections were not necessary.

Total and carbonate alkalinities were measured using the pH method (Grasshoff, 1976), in which a fixed amount of standard HCl is added to 50 ml of seawater, and the resultant pH is recorded. Eight replicate samples had a standard deviation of 0.004 meq/liter.

Materials: Reagent-grade calcite (Fisher) was reacted with seawater collected directly from Ferry Reach, a 400 m wide, 4 km long channel open to the ocean at both ends, and continuously flushed with tidal currents. Chemical analysis of the calcite is given in Table 1. The identification as calcite was confirmed by x-ray diffraction analysis, which indicated well-crystallized material of uniform composition.

Experiments in Closed Systems

Introduction: A number of experiments involved the addition of weighed increments of reagent-grade calcite to samples of 5 to 50 milliliters of fresh seawater from Ferry Reach. Some of these experiments were in the style of classical carbonate saturometry as originally introduced by Weyl

(1961). A 10 mm internal diameter centrifuge tube, that tapered toward its closed end, made possible pH measurements with a few milliliters of seawater, if the electrode was lowered as far as possible into the tapered part of the tube.

The simplest experiment was the addition of excess calcite to the system, so that the settled calcite mud covered the electrode to a depth of several centimeters. pH was then recorded as a function of time, and it was assumed that the reactions in the calcite-seawater system were isolated from the external atmosphere, and even from the supernatant seawater.

In a second type of experiment, the reagent-grade calcite was added to the centrifuge tubes in increments, and the pH recorded for each increment until a constant value was achieved.

A third type of closed system experiment involved addition of various weights of calcite to fixed volumes of seawater in stoppered pyrex flasks. The flasks were continuously shaken on a shaker table, and measurements of pH made at increasing time intervals.

Precautions: Although several experiments in closed systems were successful, the experimental difficulties are such that we did most of our work in systems equilibrated with the P_{CO_2} of the Bermuda atmosphere. If the seawater was not poisoned with $HgCl_2$, CO_2 production from organic materials in the seawater caused lowering of pH in excess of that caused by carbonate precipitation. Even if the water was treated with $HgCl_2$, bacterial action was apparently not entirely halted at Hg concentrations ordinarily deemed sufficient to inhibit biological activity. We were always in doubt as to whether we had added enough Hg, or whether we had added so much that it interfered with the carbonate reactions. At any rate, a slow drift of pH downward occurred in many experiments. Also, in experiments in centrifuge

tubes, the system was not truly closed, and CO_2 escaped into the atmosphere at a rate sufficient to invalidate experiments lasting longer than an hour or two. Finally, we observed what seems to be an influence of carbonate particles on the pH electrode. Calcite-seawater systems, as well as natural carbonate sediment-seawater systems, typically yielded pH values in the settled sediment different from those in the supernatant seawater. If a bottle with sediment was shaken, and the pH then measured at the bottom of the bottle as the sediment settled, the pH usually diminished as the sediment accumulated and compacted. We suspect that CO_2 is adsorbed on the carbonate particles, but have not by any means established the validity of this suggestion.

Results: Despite these difficulties, some of the experiments in closed systems produced useful results. The procedures of calculation and measured and computed values discussed below are given in the Appendix.

1. Stability of calcite: Addition of excess reagent-grade calcite to seawater in a centrifuge tube produces pH values of 7.48 to 7.50 in the sediment surrounding the electrode. Calculations from these values yield an apparent constant, (K'), $m_{Ca^{++}} m_{CO_3^{=}}$, for calcite of $10^{-6.29}$, which corresponds, according to our conversions of concentrations to activities, to a K ($a_{Ca^{++}} a_{CO_3^{=}}$) of $10^{-8.5}$. These values are in excellent agreement with values of K' for pure calcite determined by Ben-Yaakov and Goldhaber (1973) and values of K determined by Christ, et al. (1974). Berner (1976) obtained a K' of $10^{-6.23}$ and a K of $10^{-8.45}$, slightly larger values but consistent in their difference.

2. Solubility of precipitates on reagent-grade calcite as a function of "relative thickness", i.e., weight of precipitate formed per gram of calcite: It has been known for a long time that addition of a small amount

of reagent-grade calcite to typical surface seawater causes a lowering of pH, and a second addition lowers the pH still further. After each addition a record of pH with time shows that the pH values achieved are constant. Chave (1965) and Chave and Suess (1967) apparently assumed that the carbonate precipitated by the lowering of pH is a low magnesian calcite with a solubility like that of calcite, and that the system is prevented from attaining equilibrium with this precipitate because organic matter stops the reaction. Weyl (1965), on the other hand, showed clearly that precipitates of different and higher solubilities than calcite can be formed on calcite. Berner (1975) shows an electron photomicrograph of a high magnesian calcite (~ 7-10 mole % $MgCO_3$) that he grew from supersaturated seawater on low magnesian calcite seeds. High magnesian calcites, although their solubilities are not well established, are more soluble than nearly pure calcite. We have taken the stand, for reasons to be given later, that the small lowering of pH to a constant value caused by addition of a small amount of reagent-grade calcite to seawater is, indeed, the result of the precipitation of a carbonate more soluble than calcite.

Figure 1 shows the results of experiments in closed systems, in which the constant pH values achieved after additions of calcite to seawater are plotted against the weights of calcite added per cm^3 of seawater. Figure 2 shows the "relative thickness", i.e., micromoles of carbonate precipitated per gram of calcite added to the solution, as a function of the negative log of the ion activity product of Ca^{++} and $CO_3^{=}$ in the solution, -log (IAP). This form is a matter of convenience; the composition of the precipitate is unknown, so its activity product cannot truly be calculated. A question also arises concerning the achievement of equilibrium between precipitate

and solution. Thus, a calculated IAP for $CaCO_3$ serves principally to illustrate the change in the amount of dissolved carbonate in the solution as a function of the average thickness of the precipitated layer.

Further discussion of closed systems will be postponed until the open system work has been described.

Experiments in Open Systems

General: Because of the difficulties encountered in our studies of closed systems, we did most of our work in solutions equilibrated with the Bermuda atmosphere. One requirement of this method is that the P_{CO_2} of the atmosphere be known, or at least it is necessary to know its variations with time. P_{CO_2} of the local atmosphere was tested by bubbling air through a sample of seawater with measured carbonate alkalinity and continuously recording the pH of the sample. pH variations during most of these experiments were very small, about 0.02 pH units. During the investigation we found P_{CO_2} levels in the laboratory air as high as 500 ppm. Even with an air source outside the laboratory, we found significant contamination from the exhausts of air conditioners until we moved the intake of the aquarium pump well away from the laboratory building. The average P_{CO_2} of Bermuda air during August, 1978, calculated from the pH and alkalinity of the equilibrated seawater, is somewhat below the world average; 320 ppm by volume. Despite the good stability of our pH meter, the accuracy of the CO_2 determinations is probably $\pm$ 15 ppm.

Stability of calcite: The stability of the reagent-grade calcite was determined in the open system by placing 15 or sometimes 20 milliliters of seawater in a plastic tube fitted with a fritted glass disk at the bottom.

Air from an aquarium pump located outside the laboratory was first bubbled through seawater, which served to saturate it with water vapor, as well as to act as a monitor for P_{CO_2} of the air. The air was then passed up through the disk to agitate the seawater in the plastic tube. Tests showed no sensitivity of the pH measurement to bubbling rate. After equilibration of the seawater with air, determined from a constant pH of the recorder record, an excess of reagent-grade calcite was added to the system. The pH achieved (7.86) is consistent with a pK' of 6.29 and a pK of 8.50, as obtained from the constants and calculation procedures given in the Appendix.

IAP_{CaCO_3} vs. relative thickness: As in the closed system, increments of reagent-grade calcite were added to 15 milliliters of seawater equilibrated with the atmosphere. Again pH was plotted against weight of calcite added (Fig. 3) and -log IAP_{CaCO_3} of the solution was plotted versus "relative thickness" (Fig. 4). The results of closed system experiments opened and re-equilibrated with air are also shown on Fig. 3.

Combined experiment: Figure 5 is a plot of -log IAP_{CaCO_3} versus relative thickness of the precipitated layer for experiments in which calcite is first equilibrated in closed systems, then the systems are opened to the atmosphere by bubbling air through them. For comparison, the plot also includes the results of the closed and open system experiments referred to above. When reagent-grade calcite is added to a closed system, carbonate is precipitated by reaction with both carbonate ion and bicarbonate ion. Reaction with bicarbonate ion generates CO_2 according to

$$Ca^{++} + 2HCO_3^- = CaCO_3 + CO_2 + H_2O.$$

The P_{CO_2} rises to about 4 times the original value. When the system is opened CO_2 is swept out, $CO_3^=$ ion increases, and more $CaCO_3$ is precipitated. At the end of the cycle, carbonate alkalinity is reduced to less

than half its original value. The thickness versus -log IAP curves for the precipitates formed in the closed system, in the system that was opened after being "closed", and in the system open from the beginning, show similar functional relations between -log IAP and relative thickness (Fig. 5).

Aragonite

Only one set of seawater experiments was run with aragonite. Berner (1975) showed that the behavior of aragonite in seawater is not affected by the presence of magnesium. Our experiments consisted of putting Hg-poisoned seawater into closed flasks with various weights of acid-washed, ground (< 62 μm) aragonite (0.1 to 1.0 g in 20 ml) obtained from the coral Diploria sp. The flasks were continuously shaken on a shaker table and the pH of the suspensions was monitored as a function of time. Flasks containing more than 0.3 grams of aragonite gave a final pH of 7.71 after reaction, which corresponds to a pK of 8.31, between the value of 8.36 for pure, well-crystallized aragonite obtained by Siebert, et al. (1974), and the value of 8.28 determined by Berner (1976). The flasks with 0.3 and 0.1 g aragonite yielded constant values as much as 0.1 pH units higher than those with higher solid to solution ratios, suggesting that precipitation of a relatively thick layer of new carbonate on aragonite results in structural or compositional differences that make the precipitated carbonate a little more soluble than aragonite. In any case, the effect of the precipitate thickness on -log IAP_{CaCO_3} is much less important for aragonite than for calcite.

Discussion of Open and Closed System Experiments

The graphs of -log IAP_{CaCO_3} versus relative thickness of the precipi-

thickness at a poorly-defined value of about 7.9. The limiting value of -log IAP is not as accurate for the closed system experiment because no data were obtained for small additions of calcite to seawater. Nevertheless, the value of 7.9 corresponds to a supersaturation relative to calcite expressed in terms of $\log \frac{IAP}{K_{calcite}}$ ($\log \Omega$) of 0.6 (400%). Berner (1975) found that a supersaturation of about this amount or more was necessary for the growth of small quantities of carbonate on calcite seeds in seawater (0.1-1.8 g calcite seeds/liter seawater). He also showed that the carbonate grown at a constant supersaturation of about $\log \Omega = 0.7$ (500%) was a 7-10 mole % magnesian calcite.

We conclude that calcite grains, exposed to supersaturated seawater, grow a layer of progressively more soluble carbonate. The upper limit of solubility of the outer surface of this layer is at a -log IAP of about 7.9 (Fig. 5). This value for $-\log (a_{Ca^{++}} a_{CO_3^{=}})$ in seawater corresponds to a pH of about 8.2 for surface seawater of average alkalinity--the pH generally accepted as representative of the temperate and tropical surface oceans. If surface seawater achieves higher pH values, the surface layer on the calcite should increase in thickness at constant solubility, tending to return the pH to 8.2. Berner, by maintaining a constant supersaturation of $\log \Omega = 0.7$, achieved a continuous increase of thickness at constant composition. From the work of Berner and that of Weyl (1965), it seems clear that the decrease in -log IAP of the $CaCO_3$ component of the precipitated layer is caused chiefly by increasing Mg content. The maximum solubility achieved undoubtedly is controlled by the Mg content of seawater--a higher Mg/Ca ratio might well result in precipitation of a more soluble magnesian calcite with a higher Mg content.

We find it difficult to sustain arguments against the achievement of metastable equilibrium between seawater and added calcite in our experiments. The arguments for metastable disequilibrium, based on interference of organic matter or another surfactant, are countered by our experiments in which calcite was first equilibrated in closed systems and then in open systems. For a given closed system experiment, the amount of carbonate precipitated in the closed system became constant, and held that constancy for several days. When the system was opened, and the excess CO_2 was swept out of the system by air, much more carbonate was precipitated, showing that the carbonate surface was entirely receptive to more precipitate when the $CO_3^=$ in the solution was increased. Furthermore, when the system was opened, and more precipitate was formed, the -log IAP of the solution decreased because of the increased solubility of the thicker precipitate.

Figure 5 shows that all the precipitation experiments have the same functional relation between the amount of carbonate precipitated per gram of calcite added, and the activity product of calcium and carbonate in the resultant solution. The activity product in the solution increases with increasing thickness, and reaches an asymptote at a rather poorly defined -log IAP value of about 7.9.

This similarity in functional relationship is independent of whether precipitation on the calcite added took place in separate containers with different weights of calcite, or whether the precipitation took place in a single container on successive additions of calcite. This result means that the "solubility"--relative-thickness relation is nearly independent of the pathway used to achieve it.

Thus, a small addition of calcite to calcite-supersaturated seawater results in a relatively thick layer of precipitated carbonate. The reacted

seawater is presumably saturated with respect to the $CaCO_3$ component of the outer portions of this layer (not necessarily in total equilibrium as a solid solution). A second addition of calcite lowers the pH of the seawater again, and produces precipitated carbonate with a solubility of its outer surface lower than that for the first increment. We conclude that part of the first precipitate must dissolve and reprecipitate on the second increment of calcite, because the outer portion of the carbonate of the first increment has a solubility greater than the solubility of the final surface exposed to the solution after the second increment. Thus, the system reaches its metastable equilibrium by precipitation on the second increment, and by dissolution of part of the layer of carbonate precipitated on the first increment. This sequence of events is necessary if the incremental additions to the open system are to give the same basic results as individual open systems with different initial calcite additions.

The importance of this argument is that the relatively highly soluble carbonates precipitated on calcite from calcite-supersaturated seawater are responsive to decreases in the supersaturation of that seawater and dissolve to produce other carbonates more soluble than calcite in the less supersaturated seawater. The preceding statement means that in the surface seawater-suspended solid system of the mixed layer of the ocean, there are solids that will respond to decreases in the supersaturation of that system with respect to calcite by dissolving, and thus must be considered as sinks for atmospheric carbon dioxide.

Dissolution Experiments

To test the reactivity of the carbonate layer precipitated on calcite in supersaturated seawater, several qualitative experiments were performed.

One gram of the reagent-grade calcite used in the preceding experiments was added to a liter of seawater equilibrated with Bermuda air. In one experiment the initial pH of the seawater equilibrated with air was raised to 8.30 with sodium carbonate solution; in the other the pH was 8.19, that of the natural seawater in equilibrium with the Bermuda atmosphere. The final pH of the first experiment, after the addition of one gram of calcite, was 8.14; that of the second experiment, 8.12. These pH values, in the open system, correspond to -log IAP values of 7.96 and 8.00, respectively. The calcite, therefore, was coated with a layer of carbonate, the outer part of which possessed a solubility higher than that of calcite (-log K = 8.50) or aragonite (-log K = 8.31). The coated calcite was then separated from the seawater by filtration, and while still damp was added to 10 ml of Ferry Reach seawater equilibrated with Bermuda air and adjusted to pH 7.88 (very nearly a solution in equilibrium with pure calcite at pH 7.86). The pH of the first solution rose to 8.02, that of the second to 8.00. The experiments lasted 24 hours; the pH was not entirely constant, and was still creeping upward at a very low rate at the termination of the experiment.

The first conclusion that can be drawn from these experiments is that the carbonate precipitated on calcite from supersaturated seawater reacted with seawater saturated with calcite, and dissolved to produce a pH (8.0) higher than those in equilibrium with calcite or aragonite (7.86 and 7.95, respectively). The second conclusion is that the observed pH (and IAP) is considerably lower than one might have predicted from the solubility calculated for most of the carbonate precipitated on the calcite treated with seawater. A pH of about 8.1, corresponding to a -log IAP of about 8.0, would be a reasonable prediction for the result of addition of the gram of seawater-treated calcite. The lower pH found (pH = 8.0 and -log IAP = 8.2) we cannot explain. It is conceivable that the rate of solution of the magnesian

calcite precipitated on the calcite is extremely slow because of inhibition by phosphate (see Hanor, in press), but more experimental work is necessary to resolve the anomaly.

Conclusions

Additions of nearly pure calcite to Bermuda seawater initially supersaturated with calcite and aragonite produce a surface film of carbonate on the calcite that is more soluble than calcite. The negative logarithms of the product ($a_{Ca^{++}} a_{CO_3^{=}}$) for this carbonate range from about 7.9 for thick films deposited from high pH seawater to 8.5 (the pK for pure calcite) for thin films precipitated on large surface areas at pH values representing near-equilibrium with calcite. The increase of solubility of the film is probably correlated with increasing Mg content of the precipitated carbonate. The most convincing demonstration of increased solubility with increased thickness of precipitated film comes from experiments in which the IAP for $CaCO_3$ of the seawater was first decreased by addition of calcite and precipitation of carbonate in a closed system, then increased by opening the system to the atmosphere and thickening the precipitate on the solid.

Experiments designed to test the solubility of the precipitates by dissolving them to equilibrium gave equivocal results. On the one hand, the precipitates exhibited a solubility greater than aragonite or calcite; on the other hand, the solubilities are less than predicted. However, these experiments do demonstrate that the precipitates react rapidly in undersaturated seawater.

Furthermore, as the concentration of CO_2 in the atmosphere increases, and the CO_2 content of the ocean mixed layer also increases, carbonate coatings on calcite should begin to dissolve before aragonite or calcite. Further investigations are necessary to determine the importance of the coatings in the global balance of carbon dioxide, but it is clear that models that assume no uptake of CO_2 by reaction with solids until aragonite undersaturation is reached may be significantly in error.

TABLE 1

Chemical Analysis of Fisher Calcite

Component	Percent
$CaCO_3$	100.02
SO_4	0.002
Ba	0.003
Ce	0.0005
Fe	0.0007
Heavy metals (as Pb)	0.0007
Sr	0.04
Mg	0.004
K	0.003
Na	0.02
Insoluble in HCl	0.005

Figures

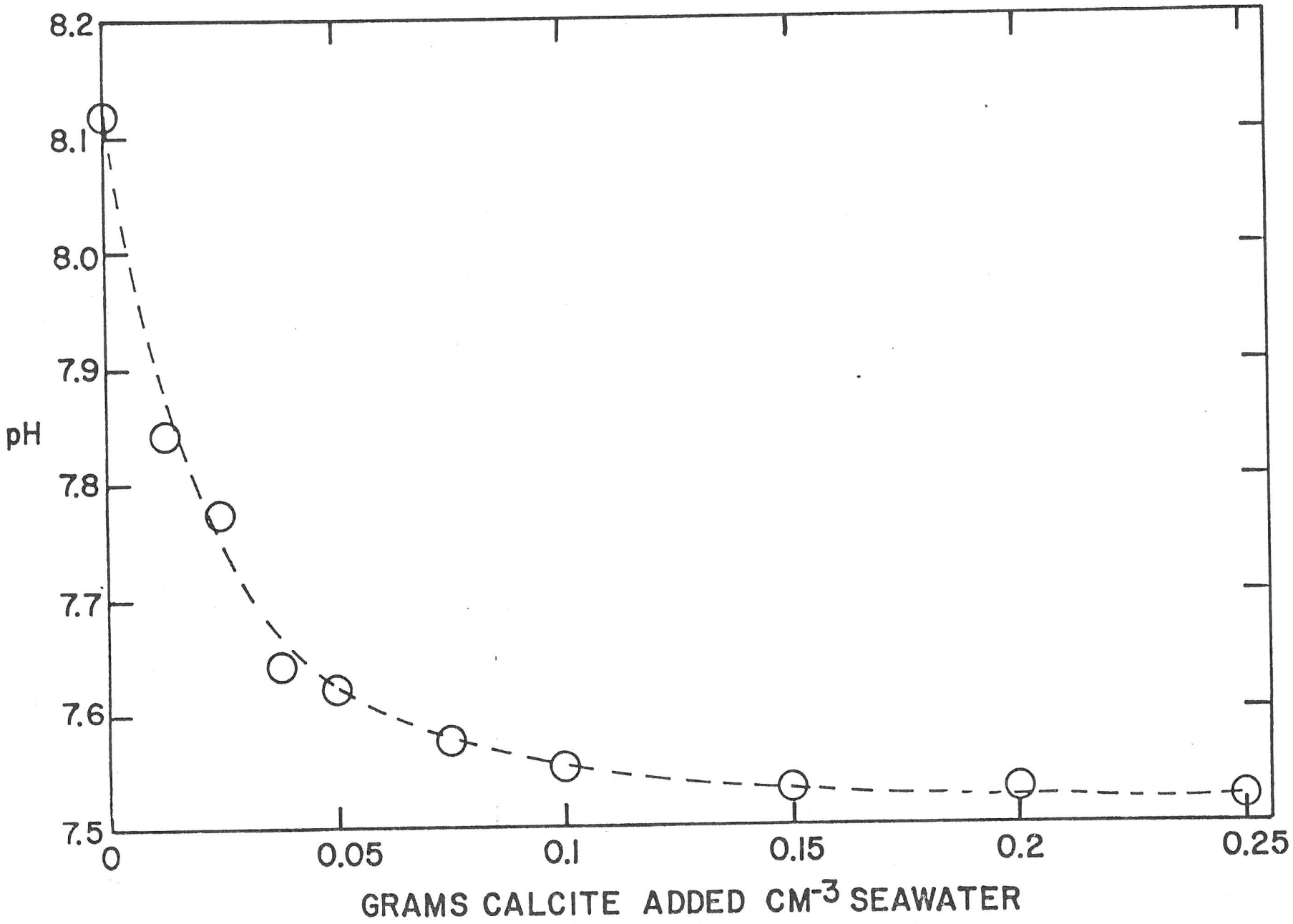
Fig. 1. Closed-system saturometry with reagent-grade calcite. Individual weights of calcite added to 20 cm^3 of $HgCl_2$-treated seawater in stoppered flasks. Final pH value by extrapolation equals 7.5.

Fig. 2. Negative logarithm of IAP_{CaCO_3} ($a_{Ca^{++}} a_{CO_3^=}$) as a function of relative thickness of carbonate precipitate (in μmoles of $CO_3^=$ precipitated $gram^{-1}$ calcite) for closed system experiments.

Fig. 3. Open-system saturometry with reagent-grade calcite compared to results of closed systems re-equilibrated with the atmosphere. Open system experiment represents successive additions of calcite to 15 cm^3 of seawater. Final extrapolated pH value is 7.86. Closed system experiments represent individual weights of calcite added to 20 cm^3 of $HgCl_2$-treated seawater in stoppered flasks. The closed systems were equilibrated, then opened, and re-equilibrated by bubbling air through them.

Fig. 4. Negative logarithm of IAP_{CaCO_3} ($a_{Ca^{++}} a_{CO_3^=}$) as a function of relative thickness of carbonate precipitate (in μmoles $CO_3^=$ precipitated $gram^{-1}$ calcite) for open system experiment.

Fig. 5. Comparison of functional relations between -log IAP_{CaCO_3} and relative thickness of precipitate for open, closed, closed-then-open system experiments. Notice the apparent, but crude, similarity in the results for the three experiments. The values of the stability constants (pK) for calcite and aragonite are also shown.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7.9
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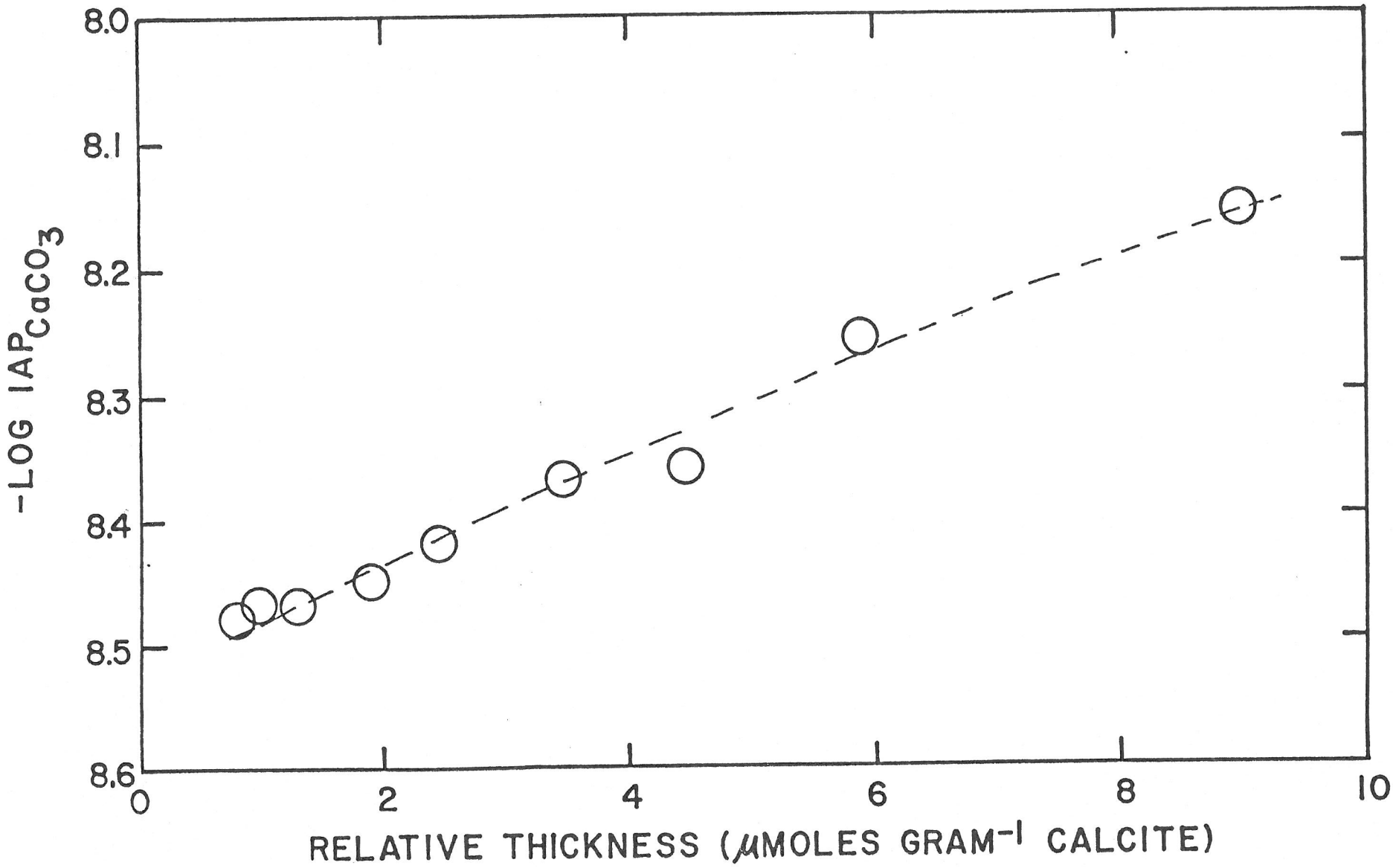
GRAMS CALCITE ADDED CM-3 SEAWATER


8.0
8.1
8.2
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8.4
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-LOG IAP$_{CaCO_3}$
0
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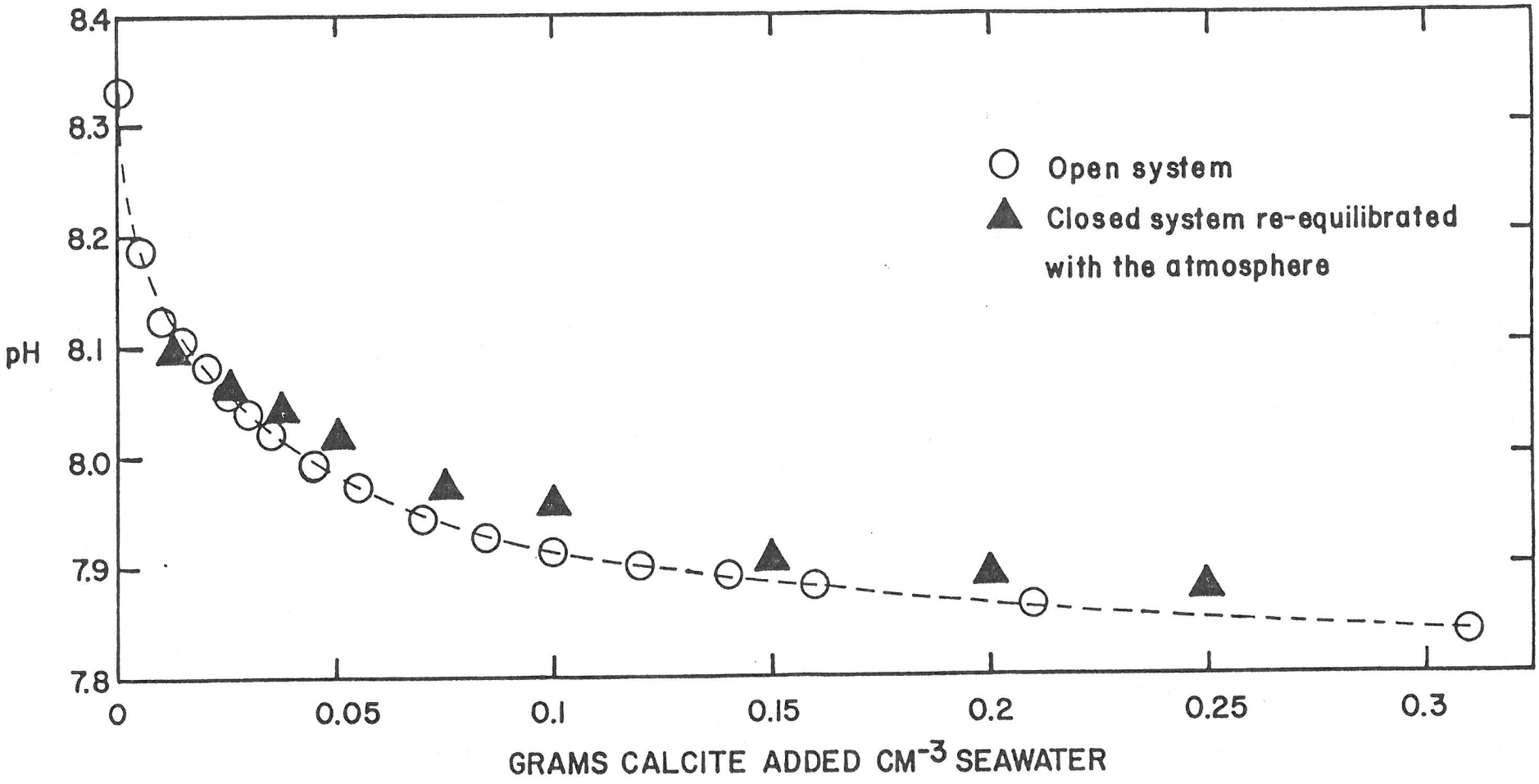
8
10
RELATIVE THICKNESS (μMOLES GRAM^{-1} CALCITE)

Fig. 2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8.0
7.9
7.8
pH
0
0.05
0.1
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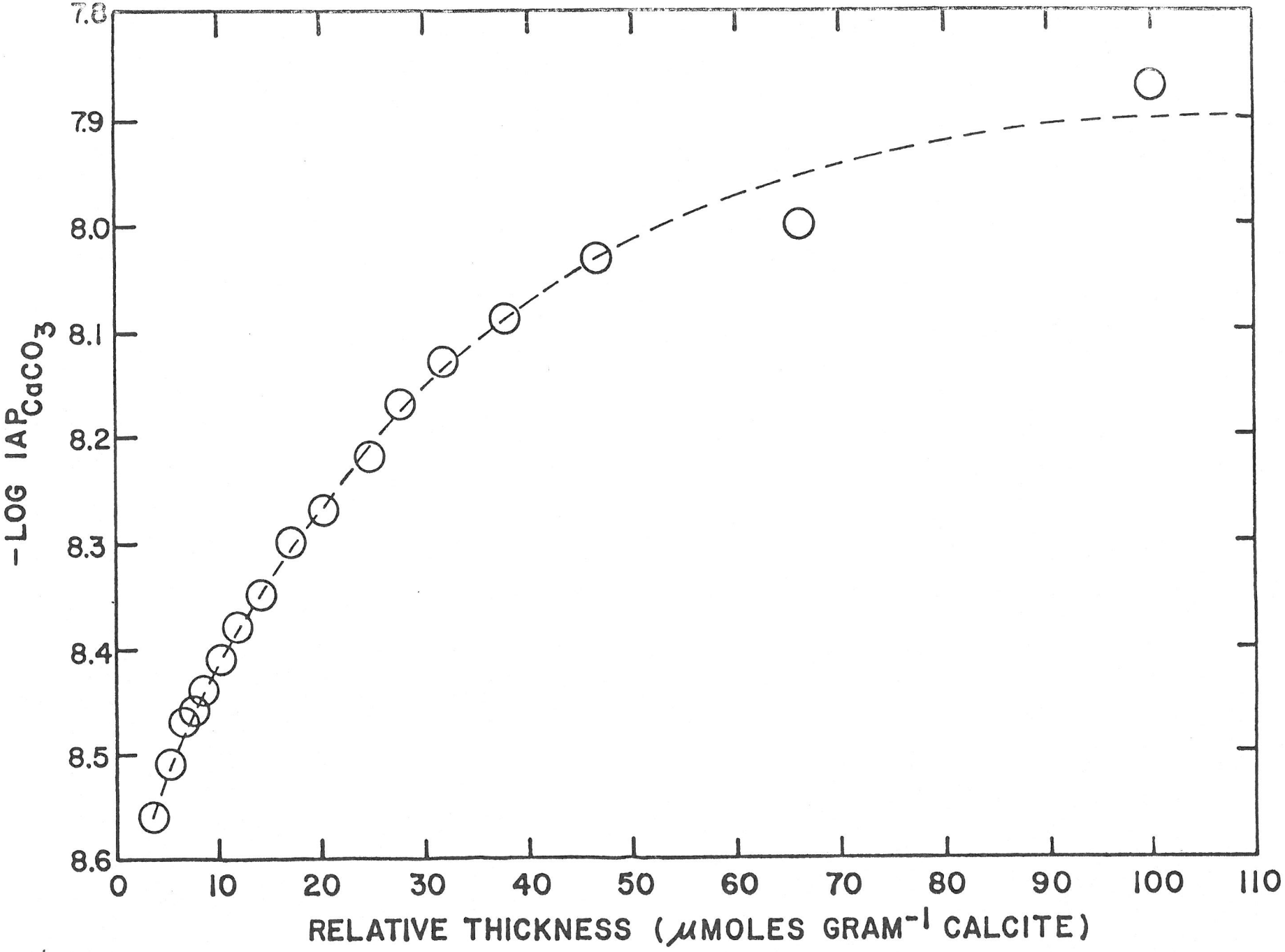
0.25
0.3
Open system
Closed system re-equilibrated with the atmosphere
GRAMS CALCITE ADDED CM-3 SEAWATER


7.8
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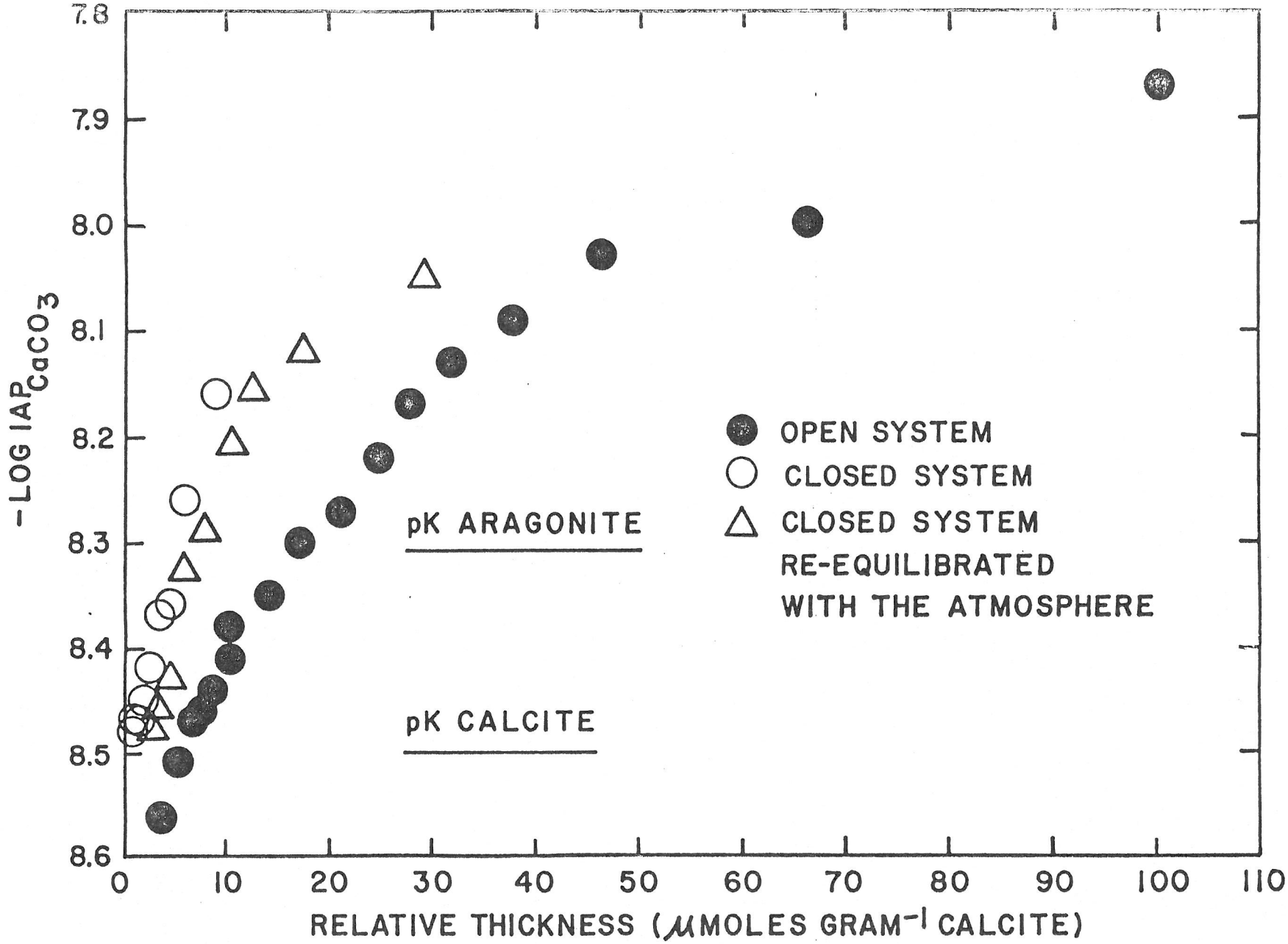
8.3
8.4
8.5
8.6
-LOG IAP$_{CaCO_3}$
0
10
20
30
40
50
60
70
80
90
100
110
RELATIVE THICKNESS (μMOLES GRAM^{-1} CALCITE)

Fig 4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8.6
-LOG IAP$_{CaCO_3}$
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10
20
30
40
50
60
70
80
90
100
110
RELATIVE THICKNESS (μMOLES GRAM^{-1} CALCITE)
pK ARAGONITE
pK CALCITE
OPEN SYSTEM
CLOSED SYSTEM
CLOSED SYSTEM
RE-EQUILIBRATED
WITH THE ATMOSPHERE

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Appendix

Constants

The constants used for the calculations are listed below. These values are a consistent set developed by Hung Chang, a graduate student at Northwestern University, who surveyed the current literature and attempted to derive a unique set of constants that would fit the thermodynamic values and the empirical K's for seawater. Although the values used are not unique, the various other consistent sets he obtained are not markedly different, in most cases they agree within about 0.02 $\log_{10}$ units. All values are for 25°C.

$$K_{\text{calcite}} = a_{Ca^{++}} a_{CO_3^{=}} = 10^{-8.50} \tag{1}$$

$$K'_{\text{calcite}} = m_{Ca^{++}} m_{CO_3^{=}} = 10^{-6.29} \tag{2}$$

$$K'_2 \text{ carbonic acid} = \frac{a_{H^+} m_{CO_3^{=}}}{m_{HCO_3^-}} = 10^{-9.09} \tag{3}$$

$$K'_1 \text{ carbonic acid} = \frac{a_{H^+} m_{HCO_3^-}}{m_{CO_{2aq}}} = 10^{-6.00} \tag{4}$$

$$K_0 \text{ carbon dioxide} = \frac{a_{CO_{2aq}}}{P_{CO_2}} = 10^{-1.47} \tag{5}$$

$$\gamma_{Ca^{++}} \gamma_{CO_3^{=}} = 10^{-2.21}, \quad \gamma_{HCO_3^-} = 10^{-0.33}, \quad \gamma_{CO_{2aq}} \cong 1$$

For Bermuda seawater:

$$m_{Ca^{++}} = 0.0109 \text{ moles/liter},$$

$$P_{CO_2} \text{ (Bermuda air)} = 10^{-3.51} \text{ atmospheres},$$

$$K'_{borate} = \frac{a_{H^+} \, m_{B(OH)_4^-}}{m_{B(OH)_3}} = 10^{-8.73} \qquad \text{and} \tag{6}$$

$$\text{total borate} = \Sigma_B = 0.434 \text{ millimoles/liter}.$$

Measurements and Calculations

a_{H^+} was measured with glass electrodes calibrated on the NBS scale and the total alkalinity according to Grasshoff (1976). The relation between total alkalinity and carbonate alkalinity is given by:

$$A_T = A_c + A_B = A_c + \frac{0.434}{1 + Q_{H^+}}, \text{ where } Q_{H^+} = \frac{a_{H^+}}{K'_B}. \tag{7}$$

From the equations given above, the following relations can be obtained:

$$m_{CO_3^=} = \frac{A_c}{(2 + a_{H^+}/K'_2)}, \tag{8}$$

$$m_{HCO_3^-} = \frac{a_{H^+} \, m_{CO_3^=}}{K'_2} = \frac{A_c}{\left(1 + \frac{2K'_2}{a_{H^+}}\right)}, \tag{9}$$

$$m_{CO_{2aq}} = \frac{a_{H^+} \, m_{HCO_3^-}}{K'_1}, \tag{10}$$

$$P_{CO_2} = \frac{a_{CO_{2aq}}}{K_o} \quad \text{and} \tag{11}$$

$$\Sigma_{CO_2} = \frac{A_c(1 + a_{H^+}/K_1' + K_2'/a_{H^+})}{(1 + 2\,K_2'/a_{H^+})} \; . \tag{12}$$

The measurements of pH and total alkalinity and the use of the above expressions permit us to describe entirely the distribution of carbonate species in the initial system.

Closed System

The precipitation or dissolution of y moles of calcium carbonate in seawater requires, for conservation of mass and charge balance, the following relations:

$$\Sigma_{CO_2} = \Sigma^o_{CO_2} + y \quad \text{and} \tag{13}$$

$$A_c = A_c^o + 2y \; . \tag{14}$$

The superscript o refers to the initial condition and y is negative for precipitation and positive for dissolution.

By combining equations (7) (12) (13) and (14) one obtains

$$y = \frac{\Sigma^o_{CO_2}\left(1 + \frac{2K_2'}{a_{H^+}}\right) - (A_T^o - A_B^o)\left(\frac{a_{H^+}}{K_1'} + 1 + \frac{K_2'}{a_{H^+}}\right)}{1 + \frac{2a_{H^+}}{K_1'}} \; . \tag{15}$$

Thus, the amount of calcium carbonate precipitated or dissolved in a closed system may be evaluated from equation (15) by measuring the final pH, if the initial total alkalinity and pH of the seawater sample are known.

If the closed system is opened and equilibrated with the partial pressure of CO_2 in the atmosphere, the measurement of the final pH reached by the system allows calculation of the distribution of carbonate species, using equations (8) to (11). Total alkalinity and borate alkalinity can be calculated from equation (7). If x represents the number of moles of CO_2 exchanged with the atmosphere and y the number of moles of calcium carbonate dissolved or precipitated we have

$$A_c = A_c^c + 2y \qquad \text{and} \tag{16}$$

$$\Sigma_{CO_2} = \Sigma_{CO_2}^c + y + x, \tag{17}$$

where the superscript c refers to the conditions previously reached in the closed system. The evaluation of A_c and Σ_{CO_2} after opening the system permits calculation of y and x.

Open System

The calculations in the open system are much simpler. Equations (8) to (12) give from a simple pH measurement and P_{CO_2} the distribution of carbonate species, carbonate alkalinity, total alkalinity and total dissolved CO_2. The measurement of total alkalinity may be used as a control.

The change of carbonate alkalinity (equation 14) gives directly the amount of carbonate precipitated or dissolved.

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